

Mo isotope fractionation in surface processes: an unwanted complication

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Molybdenum is used in alloys, steels, catalysts, colours, lubricants, etc. It is an essential element in nitrogenase and other enzymes; therefore, Mo fertilizers are used in agriculture. To trace and quantify anthropogenic Mo contaminations delivered to surface waters, a data base of the natural background variability and of anthropogenic Mo sources is essential. The use of Mo isotopic composition (MoIC) data as proxy for the oxygenation history of the oceans and atmosphere relies on the assumption of a constant, average Mo isotope signature for the Mo input to the oceans. The main supply of Mo to the oceans is the dissolved load of rivers. Thus, it is essential to discriminate anthropogenic contributions to the latter from natural background in order to constrain a pre-anthropogenic continental runoff.

Early estimates of the MoIC of the continental runoff assumed average $\delta^{98}\text{Mo}$ values coincident with silicate rocks and molybdenites (-0.1 to +0.3‰). Recent compilations of molybdenite data show a very broad MoIC variation range (-0.4 to +2.3‰) with an average of about 0.4 ‰. On the other hand, the dissolved river load is preferentially enriched in heavy isotopes, with a largely variable MoIC (0.14 to 2.4‰; Archer and Vance, 2008, Neubert et al., 2011). Several hypotheses for the observed variation were suggested. Archer and Vance (2008) proposed that soil retention of light Mo is the most important control on river water. While MoIC with negative $\delta^{98}\text{Mo}$ are abundant in soils, their variation is significant, including positive $\delta^{98}\text{Mo}$ values. Adsorption of Mo onto the suspended load during river transport is comparatively small. Based on results of natural samples and leaching experiments, Voegelin et al. (2012) concluded that incongruent dissolution of igneous crustal bedrock leads to heavy $\delta^{98}\text{Mo}$ values of the dissolved river load by preferential dissolution of early magmatic sulfides. However, a permanent bias of the total continental runoff towards a MoIC heavier than the continental crust would require a continuous net volume increase of soil and/or weathered rock, which, however, cannot be maintained over geological times. Exposed marine sedimentary rocks generally have a heavy MoIC, which is reflected in the water of rivers draining them. This suggests a predominant control of catchment outcrop weathering on riverine MoIC (Neubert et al., 2011). This leaves open the question about the fate of the light isotopes. Deep open ocean sediments are a known sink for isotopically light Mo. The mass balance can be adjusted if the relative proportion of pelagic and shallow water sedimentary rocks now exposed on continents is biased towards the latter.

The range of MoIC of riverine dissolved loads is covered by that of molybdenites and thus industrial Mo. Therefore, deciphering anthropogenic contributions from natural background variations may be difficult. The good news is that the MoIC of dissolved river loads appears to be conservative and to reflect the source area MoIC, unless a significant addition (tributary, anthropogenic) is admixed. Thus, on a local or regional scale, anthropogenic input can be identified if the MoIC of the headwaters and the river downstream differ, and the $\delta^{98}\text{Mo}$ of potential anthropogenic source is known.

Archer, C. and Vance, D. (2008) *The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans*. Nature Geoscience, 1, 597-600.

Neubert, N., et al. (2011) *The Molybdenum isotopic composition in River water: constraints from small catchments*. Earth Planet, Sci, Lett. 304, 180-190.

Voegelin, A.R., et al. (2012) *The impact of igneous bedrock weathering on the Mo isotopic composition of stream waters: Natural samples and laboratory experiments*. GCA, 86, 150-165.